

High pressure layered structure of carbon disulfide

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Solid CS₂ is superficially similar to CO₂, with the same *Cmca* molecular crystal structure at low pressures, which has suggested similar phases also at high pressures. We carried out an extensive first principles evolutionary search in order to identify the zero temperature lowest enthalpy structures of CS₂ for increasing pressure up to 200 GPa. Surprisingly, the molecular *Cmca* phase does not evolve into β -cristobalite as in CO₂, but transforms instead into phases HP2 and HP1, both recently described in high pressure SiS₂. HP1 in particular, with a wide stability range, is a layered *P2₁/c* structure characterized by pairs of edge-sharing tetrahedra, and theoretically more robust than all other CS₂ phases discussed so far. Its predicted Raman spectrum and pair correlation function agree with experiment better than those of β -cristobalite, and further differences are predicted between their respective IR spectra. The band gap of HP1-CS₂ is calculated to close under pressure yielding an insulator-metal transition near 50 GPa in agreement with experimental observations. However, the metallic density of states remains modest above this pressure, suggesting a different origin for the reported superconductivity.

I. INTRODUCTION

The crystal structure of even extremely stable molecular carbon compounds like CO₂ is known to transform radically at high pressures where, above ~ 50 GPa, the carbon coordination is found, both experimentally¹ and theoretically² to switch from two in the molecular structure *Cmca* to four in the β -cristobalite structure.^{3,4} Similar pressure-induced structural transformations can reasonably be expected to occur in a compound such as CS₂, which is the focus of the present study, and which presents obvious similarities to CO₂. Indeed CS₂ adopts at zero pressure the same *Cmca* molecular crystal structure as CO₂ at moderate pressures between 15 and 50 GPa. However, the binding in CS₂ is much weaker than in CO₂, with a smaller electronic band gap and a positive formation enthalpy of about 88.7 kJ/mol as opposed to a large negative one of -393.509 kJ/mole for CO₂.^{5,6} Thermodynamically, that makes decomposition and phase separation into elementary carbon and sulfur a thermodynamic necessity for CS₂ at equilibrium already at ambient pressure and presumably even more so at higher pressures. In spite of that intrinsic thermodynamical metastability, solid CS₂ phases do exist, clearly for kinetic reasons, and are reported at ambient pressure not to decompose in measurable times, at least below ≈ 560 K,^{7,8} a temperature rising even further at high pressures, possibly up to 1000 K at 70 GPa.⁷ At high pressures but low temperatures, X-ray data have shown evidence of structural transitions of CS₂ from the molecular phase to polymeric phases with C-S coordinations rising from two (*Cmca*) to three (CS₃) to four (CS₄),⁷ and fur-

ther. With the exception of the CS₃ phase near 20 GPa, the high pressure structural behavior has been postulated so far to be similar to that of CO₂, implying (not unreasonably) that CS₄ could be β -cristobalite. In CS₂ a detailed interpretation of high pressure experimental data is further complicated by a large amount of structural disorder, particularly in the CS₄ phase where only broad rather than sharp Bragg peaks are present in the diffraction pattern.⁷ With that rationalization of the fourfold coordinated state of CS₂ near 50 GPa through simple analogy with CO₂, density functional theory (DFT) studies have considered β -cristobalite (*I42d*, also referred to as Chalcopyrite) and tridymite (*P2₁2₁2₁*), for comparison with experimental data. Lacking sharp diffraction peaks or other distinctive features, that comparison nevertheless appears somewhat elusive. The tridymite structure shows slightly better agreement with experiment but represents a thermodynamically less likely candidate than β -cristobalite since its calculated DFT enthalpy is 0.3–0.4 eV/molecule higher.⁷ The electronic structure of either fourfold coordinated crystal structure agrees with the observed metalization in the region from 40 GPa upwards.^{7,9} Besides that, in more recent experiments performed on the high pressure metallic phases of CS₂, resistivity showed evidence of superconductivity at 4–6 K over a broad pressure range from 50 to 172 GPa.⁹

From the theoretical point of view it is of course inadequate to merely trust the analogy between CS₂ and CO₂ and extend it even to very high pressures. To expand somewhat our view we instead consider that CO₂ and CS₂ are members of a broader family of IV–VI AB₂ compounds including SiO₂, silica, and SiS₂, neither of which

is molecular at zero pressure. Silica is very well known for a number of tetrahedrally coordinated polymorphs including α -quartz, α - and β -cristobalite, tridymite, coesite, etc. Much less studied until recently, SiS_2 exhibits totally different phases starting off at zero pressure with an orthorhombic (so-called NP) crystal structure made up of edge-sharing carbon-centered tetrahedra (see Ref.10) Very recently the high pressure phases of SiS_2 were experimentally characterized¹⁰ and a whole sequence of phases HP1, HP2, HP3, were described where the tetrahedra did not disappear but simply changed their mutual connectivity.

Based on the limited available high-pressure data, solid CS_2 is at the moment the least understood member of this highly important class of solids. Even if starting at zero pressure with the same molecular $Cmca$ structure which CO_2 adopts at moderate pressure, CS_2 need not develop at very high pressures the same structures as CO_2 . To fill this remaining knowledge gap we conducted an unbiased theoretical crystal structure search to explore high pressure structures of CS_2 . This search revealed that at high pressures where the carbon coordination is four the β -cristobalite structural motif is indeed superseded by a novel, robust and unsuspected layered network of tetrahedra. Only while preparing this manuscript, fresh high pressure experimental work on SiS_2 appeared,¹⁰ reporting the very same structure, designated there as HP1. Our theoretical search now found the tetrahedra-based structure of CS_2 , which is lowest in enthalpy in a wide range of pressures from 30 to 170 GPa, to be structurally identical with HP1 structure of SiS_2 ¹⁰ (see Fig. 1). Based on this HP1 structure of CS_2 we calculated the Raman spectra and pair distribution functions and found it to agree better with experimental data than those of β -cristobalite, the high pressure structure of CO_2 . We also obtained predictions for the infrared (IR) absorption spectra, not yet available experimentally, that will hopefully serve in the future to experimentally corroborate or discard our predictions. The calculated electronic structure of high pressure metallized HP1- CS_2 GPa moreover indicates a small Fermi level density of states, questioning the intrinsic nature of the observed superconductivity.

This paper is organized as follows. In Section II we present the details of our structural search and subsequent analysis. In Section III we present the structural results of our search. In Sections IV and V we analyze the lattice dynamics, Raman spectra and electronic structure of the new phase. In the final section VI we summarize the results and draw conclusions.

II. COMPUTATIONAL METHODS

The search for low-enthalpy structures of CS_2 was carried out by exploiting an evolutionary algorithm (EA), as implemented in the USPEX code.^{11–15} The EA was run in conjunction with *ab-initio* electronic structure

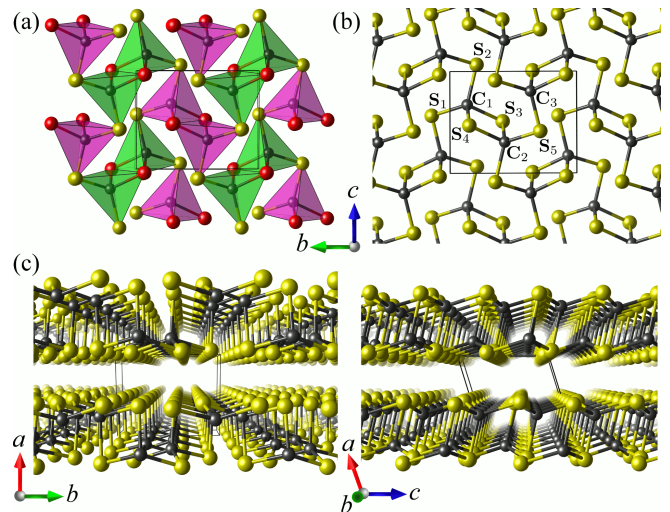


FIG. 1. (Color online) The $P2_1/c$ layered crystal structure, named HP1 after that reported for SiS_2 ,¹⁰ viewed along a , b and c -axes. Each layer is made up of two pairs of CS_4 tetrahedra. The two tetrahedra in each pair are joined by the edge, with S edge atoms shown in red. At ≈ 50 GPa the interlayer distance is about 2.1 Å. Full structural data are in Table I.

calculations and relaxations based on standard density functional theory (DFT). The Perdew-Burke-Ernzerhof (PBE)¹⁶ generalized gradient approximation as implemented in VASP (Vienna *Ab-initio* Simulation Package)¹⁷ employed the projector-augmented plane wave (PAW) method.^{18,19} The energy cutoff for the plane-wave basis was set to 550 eV to ensure full convergence. The Brillouin Zone was sampled by Monkhorst-Pack meshes with a resolution of $2\pi \times 0.05 \text{ \AA}^{-1}$. Since at low pressures the dispersion forces are important we employed for enthalpy calculations the optB86b-vdW scheme^{20,21} based on the van der Waals density functional.²² Lattice zero-point energies were not included and temperature was assumed to be zero throughout. The phonon, Raman and IR spectra were instead calculated in linear response as implemented in the QUANTUM ESPRESSO suite of programs within the LDA approximation.²³ For that, the GGA input structures were further relaxed with LDA before carrying out the phonon calculations.

Brute-force application of the EA structural search algorithm to a compound such as CS_2 with a positive formation enthalpy should lead by necessity to chemical decomposition and outright disappearance of the compound itself. As was said above, even at ambient pressure molecular CS_2 is metastable, meaning it is locally stable mechanically, and temporarily surviving due to exceedingly slow kinetics, while intrinsically unstable on thermodynamic grounds. The EA search ignores kinetics and will therefore lead to decomposition, given a large enough supercell. In this study, where we wish to find and study the high pressure metastable phases of the undecomposed compound, a strict CS_2 stoichiometry was

TABLE I. Structural data of the new phases. As seen from Wyckoff positions, the number of CS₂ formula units/cell is $Z = 4$ for all the phases except HP2 where $Z = 12$.

P=50 GPa	HP1—($P2_1/c$)					
		x	y	z	Wyck.	
	Coordinate	C	0.153	-0.355	-0.322	4e
		S	0.277	-0.091	-0.435	4e
S		0.235	0.126	0.023	4e	
Lattice	a	b	c	β	$Vol.$	
	4.86	5.59	4.74	110.02	120.95	
P=20 GPa	HP2—($P2_1/c$)					
		x	y	z	Wyck.	
	Coordinate	C	0.355	-0.133	-0.499	4e
		C	0.213	-0.365	-0.332	4e
		C	-0.061	0.362	-0.336	4e
		S	-0.438	-0.105	0.412	4e
		S	0.067	-0.131	0.423	4e
		S	0.415	-0.374	-0.419	4e
		S	0.275	-0.133	-0.243	4e
		S	-0.079	-0.388	-0.412	4e
	S	0.227	0.388	-0.251	4e	
	Lattice	a	b	c	β	$Vol.$
	6.21	6.42	11.49	105.01	442.17	
P=10 GPa	NP—($Ibam$)					
		x	y	z	Wyck.	
	Coordinate	C	0.000	0.000	0.250	4a
		S	0.122	-0.206	0.000	8j
	Lattice	a	b	c	α, β, γ	$Vol.$
	6.96	5.09	4.83	90	171.21	

assumed with an EA cell chosen to contain 12 atoms, i.e. four CS₂ molecular units. Even if small, that cell is actually still large enough to show decomposition and phase separation into carbon and sulfur in an unrestricted EA search. We therefore artificially prevented decomposition by constraining the EA search to avoid the formation of C—C and S—S first-neighbor bonds. This allows to find the high pressure crystal structures where decomposition, total or partial, is artificially suppressed. It should be noted that while the artificial nature of this constraint is such that it may endanger the formation of some denser structures at higher pressures, still various octahedral structures were also created, but their calculated enthalpies were considerably higher with respect to the tetrahedral ones. Therefore, we will by construction limit ourselves to explore metastable structures with coordination larger than four. With this constraint, the crystal structure search was performed at 0, 26, 38, 75, 120, and 170 GPa. The EA initial population (the number of structures in the starting generation) was set to 120, a large number chosen in order to densely sample the configuration space of the random search, later reduced to 30 in the following generations.

III. CRYSTAL STRUCTURES, PAIR CORRELATIONS AND X-RAY DIFFRACTION SPECTRA

The EA search produced a large variety of structures. In particular, near $P = 0$ we reproduced the known molecular *Cmca* structure, validating the scheme. Since experimentally the CS₄ tetrahedral structure was created at 30 GPa,⁹ we further focused on search for tetrahedral structures at pressures above 26 GPa. In Fig.2 we present a selection of low-enthalpy phases, that is molecular *Cmca*, and among the non-molecular, α - and β -cristobalite, compared with the tetrahedra-based phases HP1 and HP2. To complete the comparison, we also added in the α -quartz structure well known from SiO₂. While as explained above all these structures are metastable against decomposition, those which we will describe are at least mechanically stable under structural optimization and dynamically stable as shown by phonon calculations (see e.g., Fig. 6), thus representing local enthalpy minima. At any given pressure these phases compete, so they are all doubly metastable except for that with lowest enthalpy. It makes sense to consider them all anyway, as that broader picture clarifies the relative stability margins – and also because metastable phases commonly appear experimentally for kinetic reasons.

Except for 0 GPa where molecular *Cmca* was found to prevail in agreement with experiment, the most important structure obtained by the EA search at high pressures was the $P2_1/c$ (HP1). This monoclinic layered structure is quite interesting. We optimized its structure at 50 GPa and found the structural parameters as listed in Table I. As shown in Fig. 1 the carbon coordination is four, but is quite different from β -cristobalite. Each layer consists of four CS₄ tetrahedra, or more accurately two pairs of tetrahedra. Tetrahedra of different pairs (different colors in Fig. 1) share a corner sulfur, but two tetrahedra in the same pair (same color) share an edge, made up of two sulfurs. Simple as it looks, this structure came in at first as a total surprise—we designated it as “shahabite”, in the lack of an existing name. We found subsequently that the very same structure has been very recently¹⁰ observed and called HP1 in the phase diagram of SiS₂, at the much lower pressure of 2.8 GPa (actually, it had apparently been observed in SiS₂ long time ago²⁴ but not resolved).

In Ref.10 another monoclinic phase with the space group $P2_1/c$ denoted as HP2 was observed to follow HP1 at pressure of 3.5 GPa in SiS₂. Unlike the HP1, which is layered and involves four CS₂ units, the HP2 phase consists of 12 CS₂ units, arranged in a 3D covalent network. For the sake of completeness we calculated enthalpies in CS₂ for optimized HP2, and for the chain-like orthorhombic phase with space group *Ibam* which was denoted in Ref.10 as NP, the structure of SiS₂ at ambient pressure. The structural parameters of these theoretical CS₂ phases (HP1, HP2 and NP) at various relevant

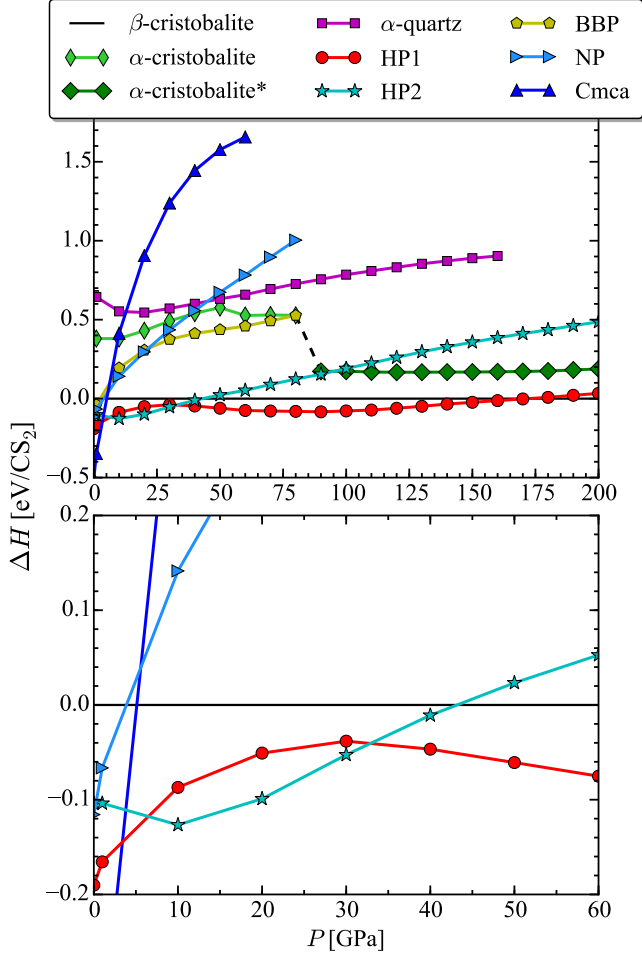


FIG. 2. (Color online) Zero temperature enthalpy for some optimized structures of CS_2 , plotted relative to β -cristobalite ($I\bar{4}2d$). No structures with carbon coordinations of three or larger than four are considered. Structures HP1 ($P2_1/c$), HP2 ($P2_1/c$) and NP ($Ibam$) are based on CS_4 tetrahedra. The relative stability of HP2 between 10–30 GPa is marginal and possibly unreliable. α -cristobalite* ($P2_12_12_1$ (No. 19)) is a high pressure version of regular α -cristobalite ($P4_12_12$ (No. 92)) where symmetry is reduced through a rotation of the tetrahedral environment of carbon atom.

pressures are listed in Table. I. Among phases not shown here and not further discussed is tridymite, also considered by Ref.7, which we found at 50 GPa to be unstable, spontaneously converting into a low-symmetry structure.

The relative enthalpies calculated for these structures are shown in Fig.2. The $Cmca$ molecular phase prevailing at low pressures is quickly supplanted by $I\bar{4}2d$ β -cristobalite at about ≈ 10 GPa. At the same time, however, the $P2_1/c$ tetrahedra-based structures appear, preempting this transformation and replacing the $Cmca$ molecular structure already at about 5 GPa. Upon increasing pressure, the two structures HP1 and HP2 remain nearly iso-enthalpic up to 30 GPa. Above that pressure the HP1 layered structure clearly prevails, its en-

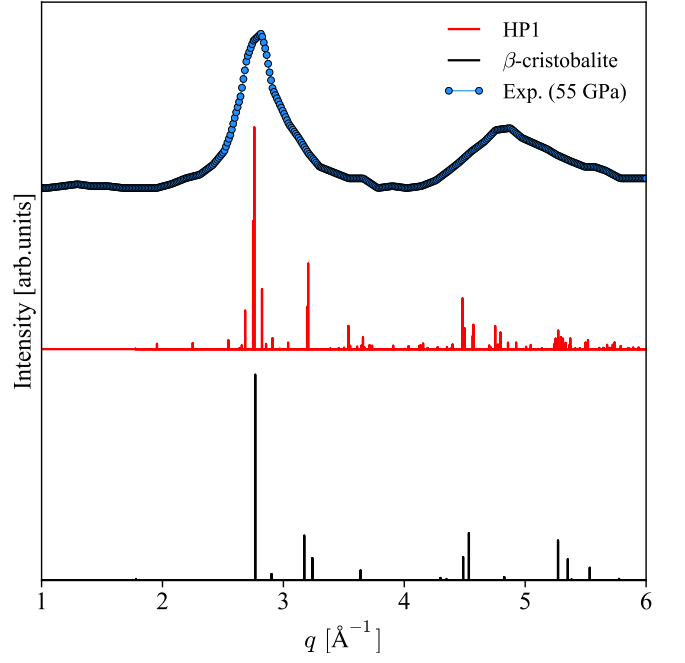


FIG. 3. Calculated X-ray diffraction patterns of the HP1 and β -cristobalite structures of CS_2 at $P = 55$ GPa, compared with experimental data of Ref. 7

thalpy remaining lower than that of β -cristobalite by a substantial amount, exceeding the estimated computational errors of about 10 meV/molecular unit, up until 160 GPa—a regime where, however, carbon coordinations larger than four will take over.⁷ The same HP1 structure which we found here appears in SiS_2 at much lower pressures than in CS_2 as is natural given the shorter bond lengths and smaller compressibility of the carbon compound.

It is interesting to rationalize the finding of edge-sharing tetrahedra in high pressure CS_2 , which behaves similarly to low pressure SiS_2 whose phases consist of variously packed tetrahedra. The stability of tetrahedra-based phases in a carbon compound such as CO_2 is denied by Pauling's third rule for ionic crystals which states that carbon edge-sharing has a destabilizing effect as it brings the positive carbon ions too close together increasing their Coulomb repulsion energy. The question is then why this obstacle does not arise in CS_2 . In order to compare the importance of this effect in CO_2 and CS_2 we structurally optimized CO_2 in the HP1 structure at 50 GPa. In agreement with Pauling, we found for this structure a much higher enthalpy of 0.4 eV/molecule with respect to the stable phase β -cristobalite, showing that edge-sharing in CO_2 is indeed unfavorable. To confirm that this is due to ionicity we calculated Bader charges^{25,26} for the C, S and O atoms in the HP1 structure. Strikingly whereas in CO_2 the partial charge of carbon is about +2, it turned out to be about -0.5 in CS_2 . The bond polarization in CS_2 is not only of small magnitude, but opposite to that in CO_2 . This finding ex-

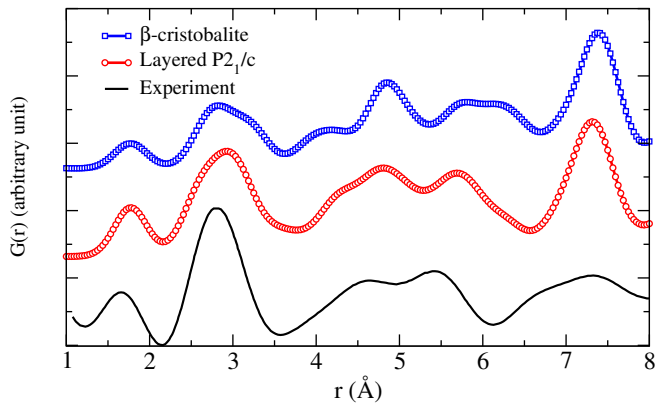


FIG. 4. (Color online) Calculated pair correlations $G(r)$ at 50 GPa for β -cristobalite (green) and layered HP1 (blue) in comparison with experimental data at 55 GPa taken from Ref. 9. An empirical Gaussian broadening was applied to the $G(R)$ of the respective perfect crystals in order to mimic the structural disorder. The Gaussian width was chosen in order to get for the C-S bond peak at 1.75 Å the same width as in experiment.⁷

plains why edge-sharing in CS_2 does not have the destabilizing effect it has in CO_2 . A second significant difference between CO_2 and CS_2 originates from the different chemistry of oxygen and sulfur which becomes relevant at higher pressures where the chalcogen binds two carbons. In this configuration, oxygen hybridizes sp^3 , favoring a bond angle of about 109° ; sulfur instead prefers p orbital binding without hybridization, and a bond angle closer to 90° . (See a detailed discussion e.g., in Ref.27). Therefore, it is not surprising to find that CO_2 should adopt the β -cristobalite structure where the C-O-C bond angles are 106° and 115° while CS_2 prefers the edge sharing tetrahedra with C-S-C bond angle of 90° .

Fig.3 shows the calculated diffraction pattern of the HP1 and β -cristobalite structures of CS_2 at 50 GPa. Comparing the position of the Bragg peaks with those of broad peaks of the X-ray structure factor $S(Q)$ in experiment at 55 GPa (Fig.3 in Ref.7) we find roughly the same agreement for both crystalline structures. In order to discuss and compare more realistically the direct-space pair correlation function, we carried out an *ab-initio* Molecular Dynamics simulation for HP1- CS_2 and β -cristobalite CS_2 at 300 K and $P = 0$ GPa, using the VASP code. Fig.4 shows the results in comparison with the experimentally extracted $G(R)$.⁷ Although differences are not dramatic, the HP1 pair correlations appear to agree with experiment somewhat better than those for β -cristobalite. As a side result, these simulations also indicated a high level of stability and robustness of HP1- CS_2 against thermal fluctuations. It is believed that this stability will be important for later tribochemical studies which we are planning.

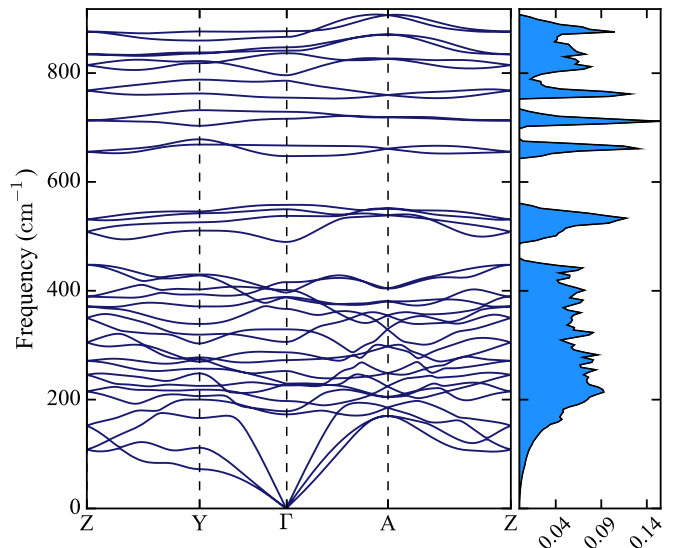


FIG. 5. (Color online) Calculated phonon spectrum of the $P2_1/c$ layered structure of CS_2 at 50 GPa.

IV. PHONONS, RAMAN, AND INFRARED ABSORPTION SPECTRA

In order to ascertain mechanical and dynamical stability, and in preparation for spectroscopy, we calculated the phonon spectrum of the main HP1 phase that dominates the phase diagram of CS_2 for a wide range of pressure. As shown in Fig. 5, at $P=50$ GPa all mode frequencies are real and positive, confirming the mechanical stability of the structure. Comparison with calculated phonons of the β -cristobalite structure⁷ shows that modes of the HP1 layered structure are slightly stiffer, although there is a fair amount of overall similarity. Phonon calculations for HP2, prohibitively expensive because of the large 36-atom unit cell, were not attempted, also given the uncertain stability of this phase.

Based on these phonon calculations, we subsequently calculated the Raman and IR absorption spectra of the HP1 structure in comparison with β -cristobalite. These spectral calculations require an insulating electronic structure. Therefore, even if available data are mostly at higher pressures, we conducted our spectral calculations at 20 GPa where both HP1 and β -cristobalite still have insulating LDA band structures. Actually, we found that LDA at 20 GPa yielded a similar volume to that of GGA at 30 GPa, and that the crystal structures underlying these LDA spectral calculations are not very different from those of our previous 50 GPa structural determinations. As shown in Fig.6 the differences between the layered HP1 and β -cristobalite predicted spectra are major. The Raman spectrum of β -cristobalite has a main (twin) peak near 300 cm^{-1} , a second main peak near 400 cm^{-1} , much weaker features near $600\text{--}700\text{ cm}^{-1}$, and nothing at higher frequencies. The HP1 Raman predicted spectrum exhibits instead a much larger peak near

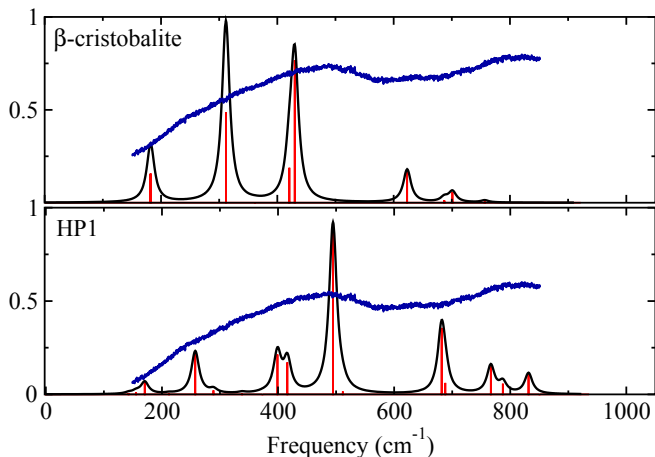


FIG. 6. (Color online) Predicted Raman spectra of two competing CS₂ structures at 50 GPa, compared with measurements at 50 GPa, 297 K.⁷ The high frequency secondary peak near 800 cm⁻¹ is only present in layered *P2₁/c* and absent in β -cristobalite. Also the low frequency spectrum is better reproduced by HP1 than by β -cristobalite.

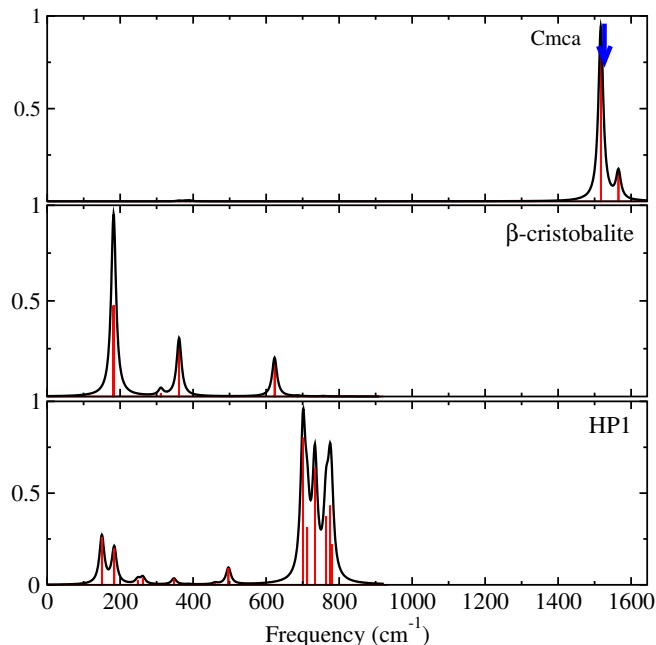


FIG. 7. (Color online) Calculated IR spectra of different CS₂ structures. Note the stiffer frequencies of layered HP1 compared with β -cristobalite. Blue arrows indicate the experimental IR peak positions of molecular CS₂.^{28,29}

500 cm⁻¹ and considerable spectral intensity at 700 and also 800 cm⁻¹. Both the 500 and the 800 features agree much better with experimental Raman data (50 GPa, 297 K).⁷ This proves that HP1 is the dominant phase of CS₂, as opposed to β -cristobalite, near 50 GPa.

Besides Raman, high pressure systems should also permit the measurement of IR absorption. We therefore calculated IR spectra, which not surprisingly turned out

to be very different for the layered HP1 and for β -cristobalite. As can be observed in Fig.7, the main predicted absorption peaks of β -cristobalite are close to \approx 200, 350 and 610 cm⁻¹. In the HP1 phase instead, after a weaker structure between 150 and 200 cm⁻¹ there is a large and broad absorption band between 700 and 800 cm⁻¹, a range where β -cristobalite should be IR silent. In future data, this unmistakable difference of IR absorption spectra should stand clearly out. Experimental IR data exist apparently only for the low pressure molecular structure. The IR peak positions observed for the *Cmca* structure represented by arrows in Fig.7 agree very well with our calculations.

V. ELECTRONIC STRUCTURE

DFT calculations yield the electron band structure of all low enthalpy phases of CS₂. All low pressure structures are insulating. The DFT-PBE electronic band structure of the layered HP1 phase is shown in Fig.8(a) at 40 GPa, above the critical metallization pressure, where the band gap of HP1-CS₂ closes. Metallization of HP1-CS₂ occurs at about 30 GPa within the PBE functional, an approximation which notoriously underestimates the gap and therefore the metallization pressure. We repeated the CS₂ calculations using B3LYP hybrid functionals, and found the metallization pressure to increase to \approx 50 GPa, a value now in excellent agreement with experiment.⁷ It is interesting to note that, owing to its initially smaller band gap than CO₂, CS₂ metallizes readily under pressure after turning from a twofold molecular state to a dense fourfold solid, unlike CO₂ which remains a wide-gap insulator long after a similar transformation into β -cristobalite. One interesting question arising at this point is whether superconductivity is predicted in the metallic high pressure state of HP1-CS₂. Unfortunately our limited resources and the large 12-atom unit cell prevented us from calculating the electron-phonon interaction λ and thus estimating the critical temperature T_c . Nonetheless, a qualitative answer to that question, even before any detailed calculations, is suggested by direct inspection of the band structure of Fig.8(c). Metallization of HP1 takes place by band overlap, with formation of a hole pocket at the $k = 0$ Γ point and of a corresponding pair of electron pockets, at k -points F and F' near A_0 and A —but off the $A - \Gamma - A_0$ line. The electron density of states of Fig.8(a) calculated after band overlap is small, not suggestive of a large electron-phonon coupling parameter λ . As in other cases, our observation of band overlap metallization³² does not offer a strong promise of superconductivity, at least of the standard BCS kind. However, the wavevectors Γ - F and Γ - F' , $\pm (0.3636, 0.0000, 0.4545)$ are electron-hole nesting vectors of HP1-CS₂ near the gap closing pressure around 50 GPa. It is possible that charge-density-wave or spin-density-wave static modulations might appear with that periodicity, possibly also accompanied by some related

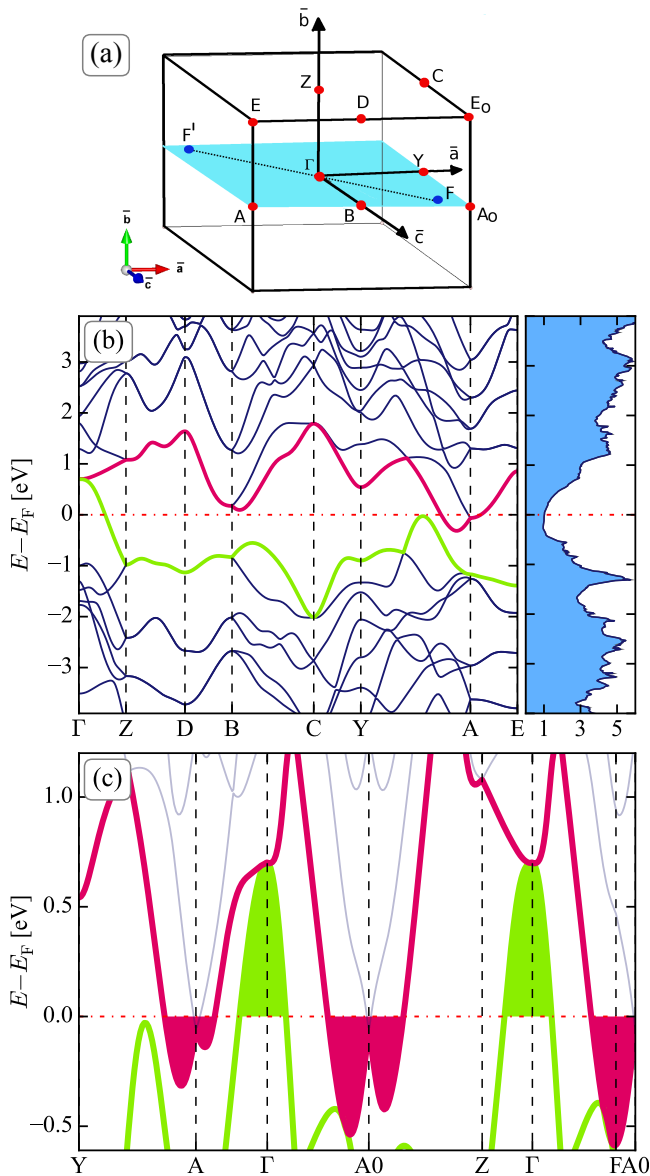


FIG. 8. (Color online) (a) The parallelepiped Brillouin zone of the HP1 $P2_1/c$ structure.^{30,31} $F = (0.3636, 0.0000, 0.4545)$ is a general point in the Brillouin zone. (b) PBE electronic structure of HP1-CS₂ at 40 GPa, above the insulator-metal transition. (c) Bands near the Fermi level showing a single hole pocket at Γ and two electron pockets at F and $F' = -F$.

superconducting phase. We are not presently in a position to inquire quantitatively into this possibility, which would require newer and different approaches.

VI. CONCLUSIONS

We presented a theoretical study of high pressure solid phases of CS₂. We discarded the obvious possibility of decomposition by restricting only to phases devoid of C-C and of S-S nearest neighbor bonds, and aiming at uncov-

ering the metastable phases of lowest enthalpy through an unbiased genetic structure search. Our main result is that, contrary to expectations based on similarity with CO₂ where twofold coordinated $Cmca$ eventually turns into fourfold coordinated β -cristobalite, high pressure in CS₂ eventually converts $Cmca$ into a different fourfold coordinated layered $P2_1/c$ phase built up of edge-sharing pairs of tetrahedra. Recently the very same structure, named HP1, has been experimentally reported for SiS₂ at much lower pressures.¹⁰ Another tetrahedra-based structure, HP2, is also stabilized between 8 and 30 GPa, but only by a small enthalpy difference with respect to HP1 comparable with our calculation errors.

The proposed HP1 structure represents a more plausible candidate structure for high pressure, fourfold coordinated CS₂ than those considered so far.^{7,9} Both calculated pair correlations and Raman spectra agree better with existing data than those of β -cristobalite. It will be a challenge for the experimentalists to try to prepare this phase in a crystalline state amenable to more accurate investigation in the future. To that end we provide substantial additional predictions, in particular of IR spectra, that should be crucial in identifying the new phase. Despite its intrinsic metastability, the HP1-CS₂ structure appears exceptionally robust. These qualities make CS₂ a good candidate system for studies of high pressure simulated tribochemistry, a project which is presently going on in the Trieste group.

Even though the layered HP1 structure is metallic above 50 GPa, it seems unlikely that it should account for the experimentally observed superconductivity,⁹ because the density of states, and therefore the dimensionless λ , is likely to remain low after the band-overlap metallic state. Although a reasonable hypothesis could be a possible partial decomposition of CS₂, with creation of some free sulfur filaments or other non stoichiometric products, we are not in a position to address that occurrence here.

We note in closing that at pressures just before metalization, where the band gap closing of insulating HP1-CS₂ is indirect, the crystal might develop a narrow charge-density-wave or spin-density-wave phase, characterized by a nesting wavevector close to $\pm F$.³³ Although there has been so far no observation of this kind in high pressure experiments, this possibility, which we also suggested for MoS₂,³⁴ seems worth pursuing.

Last and perhaps most important, our work provides a new link into the high pressure crystal chemistry of the archetypal family of IV-VI AB₂ compounds made of light elements where previously only some cross similarities between CO₂, SiO₂, and SiS₂ were discussed. We show that there is some structural kinship of CS₂ not just to CO₂ at low pressures, but eventually also to SiS₂ at higher pressures.

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